53

A PHOTOCHEMICAL MODEL OF THE MARTIAN ATMOSPHERE

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ABSTRACT. On the basis of investigation carried uptil now, the constituents of the Martian atmosphere and their relative abundance at the surface has been collected. The altitude distribution of these constituents has been calculated after considering the hydrostatic equilibrium of the atmosphere and assuming the temperature distribution with altitude in the Martian atmosphere given by Goody (1957). The photochemical modifications of the major constituents (N_2 and CO_2) are then separately considered It has been found that CO_2 is completely dissociated above 130 km and N_2 above 250 km. Considering the chemiluminescent reaction between photodissociated products and the main constituents of the Martian atmosphere, it is found that the flame bands of CO_2 and the red and violet systems of CN may be present in the Martian airglow.

INTRODUCTION

With the great progress of space research achieved in recent years, the necessity of having more information of planets and their atmospheres is felt. One of the methods of investigating the atmospheres of planets, may be to extrapolate the results obtained for the terrestrial atmosphere. For example, on determining the proton flux which is incident on the top of the earth's atmosphere causing thereby either directly or indirectly the aurora, the proton flux incident on the atmosphere of Mars may be estimated. We have considered here the atmosphere of the planet Mars. It is expected that this planet will be the first one be explored by rockets.

II VARIATION OF COMPOSITION, TEMPERATURE AND PRESSURE WITH ALTITUDE IN THE ATMOSPHERE OF MARS

The investigation of the Martian atmosphere which has been carried out uptil now, (Kuiper, 1952; Urey, 1959; Dollfus, 1951), reveals that N_2, CO_2, Ar and some amount of O_2 and H_2O vapour are present in its atmosphere.

The table below gives the composition and certain characteristics of the Martian atmosphere at its surface.

TABLE I

N_2	219.00 gm cm^{-2}
CO_2	5.98 gm cm^{-2}
Ar	1.28 gm cm^{-2}
O_2]	0.35 gm cm^{-2}
H_2O	0.042 gm cm^{-2}

Total mass of the atmosphere	227 00 gm cm^{-2}
Average surface temperature	300°K
Average pressure at the surface	8.87×10^4 dynes cm^{-2}
g at the surface	391 cm sec^{-2}

From the variation of temperature with altitude in the Martian atmosphere as given by Urey (1959) estimated from Goody's (1957) calculations, the Martian atmosphere can be divided into three regions as follows :

Region (km)	Datum Altitude Z_0 (km)	Temperature at the Datum Altitude To, (°K)	Temperature Gradient (°K. km^{-1})
0–30	0	300	−3.75
30–90	30	187.5	−0 96
90 and above	90	130	− +1.05

Assuming complete mixing of the constituents of the Martian atmosphere upto 130 km and neglecting the variation of g with altitude, the altitude distribution of the constituents has been calculated after considering the hydrostatic equilibrium. The equation is

$$n_z = n_0 \left(\frac{T_z}{T_0}\right)^{-(\bar{m}g/k\alpha+1)} \qquad \dots \quad (2)$$

where α is the rate of increase of T with height.

The mean molecular mass m has been obtained from the relative abundance given in the Table 1. The calculated distributions of N_2, CO_2, H_2O and O_2 upto 130 km are shown in Fig. 1.

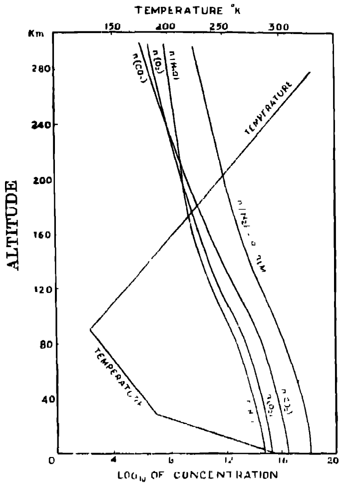

Fig. 1. The calculated distributions of N_2, CO_2, H_2O and O_2 upto 300 Km. in the Martian atmosphere.

The distribution of the constituents above 130 km, i e. in the region of diffusive separation has been calculated from the following equation :

$$\frac{n_{iz}}{n_{i+130}} = \left(\frac{T_z}{T_{130}}\right)^{-\left(\frac{m_i g}{k\alpha}+\alpha\right)} \qquad \ldots \quad (3)$$

which is obtained after replacing $\bar{m}$ by the molecular mass m_i of the i-th constituent. The distributions of atmospheric constituents of Mari above 130 km and upto 300 km are also shown in Fig. 1.

MODIFICATION OF ATMOSPHERIC DISTRIBUTION BY PHOTOCHEMICAL REACTIONS

In this section, we shall consider the distribution of the two main constituents (N_2 and CO_2) of the Martian atmosphere as modified by photochemical reactions. Due to solar ultraviolet radiations, N_2 is dissociated into two N atoms and CO_2 into CO and O. As these dissociated products are very reactive, they produce many chemical reactions leading to a complex photochemistry of the Martian atmosphere. We shall now consider separately the dissociation of N_2 and CO_2.

equation 8 and 12 the distributions of CO_2 and N_2 as modified by photochemical reactions and correct to the first approximation is calculated.

In order to obtain the distributions of N_2 and CO_2 correct to the second approximation, the transmission coefficients $K_{\nu z}$ are recalculated after assuming the above distributions of N_2 and CO_2 correct to the first approximation. The modified distributions of N_2 and CO_2 correct to the second approximation are given in Table II and in Fig. 3.

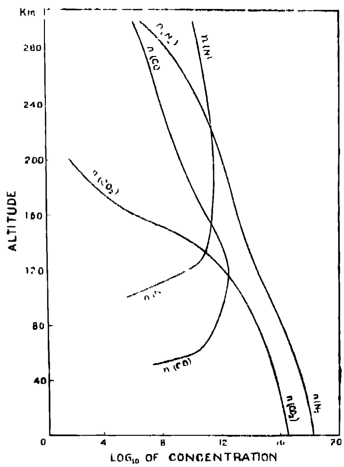

Fig. 3. The distributions of N_2 and CO_2 in the Martian atmosphere at modified by photochemical reactions.

DISCUSSION

The greatest source of error in the determination of the altitude distributions of the constituents in the Martian atmosphere is the uncertainty in the distribution of temperature with altitude. In the present calculation, the temperature distribution given by Goody (1957) has been adopted. If, however, the Martian atmosphere is assumed to be isothermal having the same temperature as at the surface, the distribution of the total particle concentration with altitude is given by

$$n_e = n_0 \exp\left[-\frac{kT}{mg} Z\right]$$

which gives the distribution as given below.

TABLE I

Altitude	nz (cm^{-3}) Isothermal	nz (cm^{-3}) Goody's Temp distribution
0	$2.14.10^{18}$	$2.14.10^{18}$
100	$2.53.10^{16}$	$1.99.10^{15}$
200	$2.98.10^{14}$	$9.30.10^{21}$
300	$3.52.10^{12}$	$7.22.10^{9}$

It is to be noted that at 300 km the total particle concentrations obtained from the two temperature distributions differ by about two orders At lower altitude the difference becomes less.

TABLE II

The distribution of N_2 and CO_2 as modified by photochemical reactions

Altitude Km	n(CO_2) cm^{-3}	n(CO) cm^{-3}	n(N_2) cm^{-3}	n(N) cm^{-3}
0	3.64×10^{16}	—	2.09×10^{18}	—
10	2.58×10^{16}	—	1.49×10^{18}	—
20	1.74×10^{16}	—	1.00×10^{18}	--
30	1.09×10^{16}	—	6.30×10^{17}	—
40	5.54×10^{15}	—	3.19×10^{17}	- -
50	2.71×10^{15}	1.93×10^{7}	1.56×10^{17}	
60	1.16×10^{15}	5.29×10^{10}	6.67×10^{16}	—
70	5.68×10^{14}	2.02×10^{11}	3.27×10^{16}	
80	3.14×10^{14}	5.74×10^{11}	1.81×10^{16}	–
90	9.78×10^{13}	1.34×10^{12}	5.71×10^{15}	-
100	3.18×10^{13}	2.22×10^{12}	1.96×10^{15}	3.28×10^{5}
110	9.60×10^{12}	2.93×10^{12}	7.23×10^{14}	6.44×10^{6}
120	9.00×10^{11}	4.08×10^{12}	2.87×10^{14}	4.33×10^{0}
130	3.00×10^{10}	2.00×10^{12}	1.20×10^{14}	1.24×10^{11}
140	7.60×10^{0}	9.13×10^{11}	5.30×10^{13}	1.90×10^{11}
150	2.44×10^{7}	2.85×10^{11}	2.46×10^{13}	2.22×10^{11}
160	9.82×10^{5}	9.49×10^{19}	1.19×10^{13}	2.64×10^{11}
170	5.39×10^{4}	3.33×10^{10}	5.92×10^{12}	2.64×10^{11}
180	3.68×10^{3}	1.23×10^{19}	3.02×10^{12}	2.65×10^{11}
190	2.81×10^{2}	4.70×10^{0}	1.56×10^{12}	2.65×10^{11}
200	2.47×10^{1}	1.89×10^{9}	8.00×10^{11}	2.57×10^{11}
210	—	7.91×10^{8}	4.04×10^{11}	2.44×10^{11}
220	—	3.42×10^{8}	1.92×10^{11}	2.22×10^{11}
230	—	1.52×10^{8}	8.35×10^{19}	1.91×10^{11}
240	—	7.00×10^{7}	3.20×10^{10}	1.52×10^{11}
250	—	3.43×10^{7}	1.13×10^{19}	1.11×10^{11}
260	—	1.62×10^{7}	1.58×10^{9}	7.92×10^{11}
270	—	8.04×10^{6}	8.59×10^{5}	5.06×10^{10}
280	—	4.08×10^{6}	2.41×10^{8}	3.36×10^{10}
290	—	2.12×10^{6}	6.58×10^{7}	2.17×10^{10}
300	—	1.13×10^{6}	1.91×10^{6}	1.44×10^{10}

TABLE III

The photon flux at the top of the Martian atmosphere and the absorption cross-section of CO_2 between 1750A—1076A.

Region $\times 10^3 Cm^{-3}$	Absorption cross-section of CO_2 cm^{2}	Photon flux cm^{-2} sec^{-2}	Region $\times 10^3$ cm^{-1}	Absorption cross-sec. of CO_2 cm^{2}	Photon flux cm^{-2} sec^{-1}
55 — 56	1×10^{-21}	6.535×10^{11}	74 — 75	$9\ 10 \times 10^{-19}$	1.055×10^{10}
55 — 57	1×10^{-21}	4.722×10^{11}	75 — 76	9.11×10^{-10}	6.034×10^{9}
57 — 58	8.52×10^{-21}	4.571×10^{11}	76 — 77	$8\ 63 \times 10^{-19}$	9.760×10^{9}
58 — 59	1.78×10^{-20}	$3\ 965 \times 10^{11}$	77 — 78	$6\ 24 \times 10^{-10}$	3.600×10^{8}
59 — 60	4.28×10^{-20}	1.945×10^{11}	78 — 79	4.57×10^{-19}	3.491×10^{8}
60 — 61	$7.04 \times 1\text{-}0^{20}$	1.889×10^{11}	79 — 80	$3\ 00 \times 10^{-10}$	$1\ 418 \times 10^{9}$
61 — 62	1.15×10^{-19}	1.821×10^{11}	80 — 81	1.70×10^{-19}	7.629×10^{8}
62 — 63	1.77×10^{-10}	1.273×10^{11}	81 — 82	9.00×10^{-20}	$3\ 254 \times 10^{8}$
63 — 64	$2\ 60 \times 10^{-19}$	$7\ 482 \times 10^{10}$	82 — 83	$6\ 00 \times 10^{-20}$	$8\ 620 \times 10^{10}$
64 — 65	$3\ 55 \times 10^{-19}$	$7\ 241 \times 10^{10}$	83 — 84	$4\ 00 \times 10^{-20}$	$1\ 919 \times 10^{9}$
65 — 66	4.59×10^{-19}	7.030×10^{10}	84 — 85	$5\ 00 \times 10^{-20}$	3.017×10^{5}
66 — 67	5.46×10^{-19}	5.426×10^{10}	85 — 86	3.00×10^{-10}	1.057×10^{9}
67 — 68	5.63×10^{-19}	2.454×10^{10}	86 — 87	2.71×10^{-18}	2.888×10^{8}
68 — 69	$5\ 87 \times 10^{-19}$	$2\ 386 \times 10^{10}$	87 — 88	9.00×10^{-17}	2.801×10^{8}
69 — 70	5.97×10^{-10}	2.320×10^{10}	88 — 89	$6\ 75 \times 10^{-17}$	2.760×10^{8}
70 — 71	6.17×10^{-19}	$2\ 308 \times 10^{10}$	89 — 90	1.03×10^{-16}	2.694×10^{8}
71 — 72	$6\ 76 \times 10^{-10}$	$1\ 538 \times 10^{10}$	90 — 91	1.92×10^{-17}	2.487×10^{8}
72 — 73	6.35×10^{-19}	6.517×10^{9}	91 — 92	3.05×10^{-17}	1.026×10^{8}
73 — 74	7.17×10^{-19}	$6\ 379 \times 10^{9}$	92 — 93	$1\ 02 \times 10^{-17}$	$9\ 621 \times 10^{8}$

The distribution of the dissociated products may be modified by chemical reactions between N_2, CO_2, CO and N· It is apparent from Figs. 3 and 1, that the effect of the dissociation of O_2 (which is neglected in the present calculation) on the distributions of CO_2, CO and O is negligible below 200 km owing to the low concentration of O_2, but becomes appreciable above this altitude. Although the concentrations of OH and H (produced by the photodissociation of H_2O by solar ultraviolet radiation below 1800A, (see Watanabe *et al.*, 1953) may be very small below 200 km but because of their reactivity the photochemistry of the Martian atmosphere can be altered considerably. Furthermore, the reactions between N, N_2, O and O_2 can produce the oxides of nitrogen, which are recently reported to be present in the Martia atmosphere (Kiess *et al.*, 1960)

TABLE IV

Distribution of N_2 molecules in the Martian atmosphere.

Altitude	n(N)	n(N) with n(hv) $\times Kv = 10^{-10}$	n(N) with n(hv) $\times Kv = 10^{-12}$	$n(N_2)$	$n(N_2)$ with n(hv) $\times Kv = 10^{-10}$	n(N) with n(hv) $\times Kv = 10^{-13}$
0	—	—	—	2.09×10^{18}	2.09×10^{18}	2.09×10^{18}
10	—	—	—	1.49×10^{18}	1.49×10^{18}	1.49×10^{10}
20	—	—	—	1.00×10^{18}	1.00×10^{18}	1.00×10^{18}
30	—	—	—	6.30×10^{17}	6.30×10^{17}	6.30×10^{17}
40	—	—	—	3.19×10^{17}	3.19×10^{17}	3.19×10^{17}
50	—	—	—	1.56×10^{17}	1.56×10^{17}	1.56×10^{17}
60	—	—	—	6.67×10^{17}	6.67×10^{17}	6.67×10^{17}
70	—	—	—	3.27×10^{16}	3.27×10^{16}	3.27×10^{16}
80	—	—	—	1.81×10^{16}	1.81×10^{16}	1.81×10^{16}
90	—	—	—	5.71×10^{15}	5.71×10^{15}	5.71×10^{15}
100	3.28×10^{5}	1.29×10^{11}	1.29×10^{10}	1.96×10^{15}	1.97×10^{15}	1.96×10^{15}
110	6.44×10^{9}	1.60×10^{11}	1.60×10^{10}	7.23×10^{14}	7.23×10^{14}	7.23×10^{14}
120	4.33×10^{9}	1.9×10^{11}	1.9×10^{10}	2.87×10^{14}	2.87×10^{14}	2.87×10^{14}
130	1.24×10^{11}	2.01×10^{11}	2.01×10^{10}	1.20×10^{14}	1.20×10^{14}	1.20×10^{14}
140	1.90×10^{11}	2.94×10^{11}	2.94×10^{10}	5.30×10^{13}	5.30×10^{13}	5.31×10^{13}
150	2.22×10^{11}	3.26×10^{11}	3.26×10^{10}	2.46×10^{13}	2.45×10^{13}	2.47×10^{13}
160	2.64×10^{11}	3.38×10^{11}	3.38×10^{10}	1.19×10^{13}	1.18×10^{13}	1.20×10^{13}
170	2.64×10^{11}	3.41×10^{11}	3.46×10^{10}	5.92×10^{12}	6.48×10^{12}	6.84×10^{12}
180	2.65×10^{11}	3.40×10^{11}	3.49×10^{10}	3.02×10^{12}	1.99×10^{12}	3.14×10^{12}
190	2.65×10^{11}	3.36×10^{11}	3.52×10^{10}	1.56×10^{12}	1.52×10^{12}	1.67×10^{12}
200	2.57×10^{11}	3.24×10^{11}	3.54×10^{10}	8.00×10^{11}	7.66×10^{11}	9.10×10^{11}
210	2.41×10^{11}	1.72×10^{11}	3.66×10^{10}	4.04×10^{11}	4.40×10^{11}	5.08×10^{11}
220	2.22×10^{11}	2.79×10^{11}	3.67×10^{10}	1.92×10^{11}	1.64×10^{11}	2.84×10^{11}
230	1.91×10^{11}	2.34×10^{11}	3.76×10^{10}	8.35×10^{10}	6.34×10^{10}	1.60×10^{11}
240	1.52×10^{11}	2.69×10^{11}	3.78×10^{10}	3.20×10^{10}	2.56×10^{10}	9.07×10^{10}
250	1.11×10^{11}	1.16×10^{11}	3.46×10^{10}	1.13×10^{10}	1.05×10^{10}	5.01×10^{10}
260	7.92×10^{10}	7.86×10^{10}	3.21×10^{10}	1.58×10^{9}	1.90×10^{9}	2.64×10^{10}
270	5.06×10^{10}	5.18×10^{10}	2.90×10^{10}	8.59×10^{8}	2.00×10^{8}	1.12×10^{10}
280	3.36×10^{10}	3.33×10^{10}	2.43×10^{10}	2.41×10^{8}	1.50×10^{8}	4.75×10^{2}
290	2.17×10^{10}	2.19×10^{10}	1.84×10^{10}	6.58×10^{7}	1.80×10^{8}	1.69×10^{9}
300	1.44×10^{10}	1.45×10^{10}	1.32×10^{10}	1.91×10^{9}	3.30×10^{8}	6.00×10^{9}

It is to be noted from Table II that above 30 km, the atmosphere of Mars is denser than the terrestrial atmosphere (Vaucouleurs has also obtained the same result, 1960). The concentrations of dissociated species (CO, O, N, OH and H) are also much higher. It is known from laboratory experiments that reactions between these constituents produce chemiluminescence and hence an airglow in the Martian atmosphere can be produced. The spectrum of the airglow is expected to contain CO_2 and CN band systems for the following reasons. It is a well known fact that CO_2 bands are emitted from $CO—O_2$ flames at ordinary temperatures. According to Gaydon (1957), such band emission may be caused by the following reaction :

$$O+CO+M \rightarrow CO_2+M$$
$$CO^*_2 \rightarrow CO_2+h\nu.$$

In the martian upper atmosphere where both O and CO are present, CO_2 band emission is therefore expected. Again, recently Broida and Heath (1957), observed a luminous reaction between CO and N emitting red and violet systems of CN. These bands of CN are also expected to be present in the Martian air glow.

In Table II the N-atom concentration has been calculated by applying eqn (13.). In this calculation, it has been assumed that every absorption of photon predissociates N_2 molecule This may not happen in reality. In order to obtain the range of concentration of N atom in the Martian atmosphere, two concentrations have been calculated for the limiting lower dissociation probabilities (10^{-12} sec^{-1} as given by Bates, 1953) and given in Table IV and from 10^{-9} sec^{-1} given in Table III.

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